

APPLICATION OF ELECTROKINETIC NANOPARTICLE MIGRATION IN THE PRODUCTION OF NOVEL CONCRETE-BASED COMPOSITES

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ABSTRACT

Electrophoresis has been widely used to build up complex composites by infiltrating particulate phases into porous ceramics and to facilitate putting uniform mineral coatings on metal for enameling. This technique uses a potential field to move charged particles that are suspended in a fluid phase into a porous medium. Fabrication generally involves a second step that fixes the layer of particles together and bonds them to the surrounding surfaces.

When electrophoresis is used to improve portland cement-based concretes or mortars, there is no easy approach to providing a densification or cementation step that will bond the resulting composite phases together. An advanced approach has been developed that uses electro-transport techniques to migrate nano-sized particles suspended in a gel or solution that can react with the matrix to produce a cementing reaction in the pore space of the mortar or concrete to form a new composite.

Electrophoretic infiltration and cementation is investigated using two types of mortar and both silicate and carbonate-based cementation. Results indicate both systems can produce useful density changes in mortar.

1. INTRODUCTION

In composite construction materials, the desirable properties, (strength, density, and durability) are related to the compactness of the material, the strength of the components, and the tenacity of the bonds that form between the constituent materials. Inorganic composites such as ceramics and concrete are typically formed with an initial porosity that is related to their granular origins. Improvements in the strength or durability are obtained by filling in the pore spaces and reducing the void space between grains (Matusinovic, Sipusic and Vrobos, 2003; Rossler and Odler, 1985; Roy and Gouda, 1973). The density increase adds to the strength (Fig. 1), but more significant strength increases and increased durability are obtained if the infilling phases can be made to cement into the granular network. The cement not only joins the infilling grains to the original grains forming the network, but provides additional volume to fill more voids.

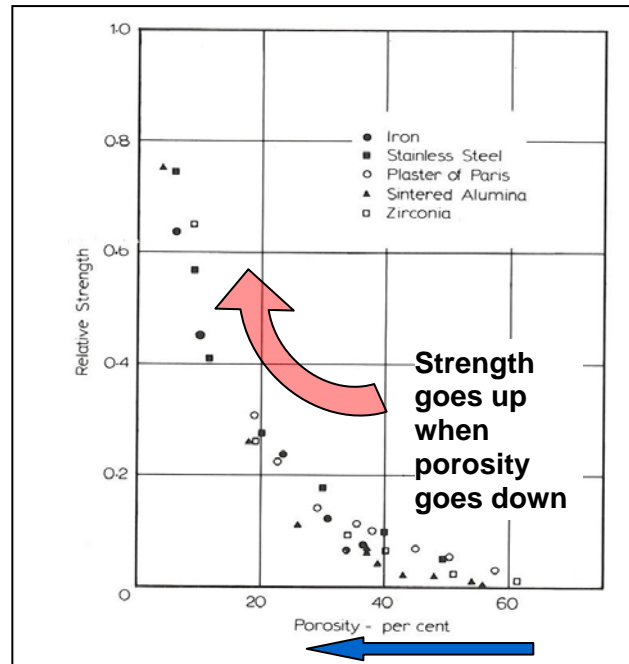


Fig. 1. Relationship between density or porosity and strength in materials (modified from Neville, 1981).

Electrophoresis has been widely used to build up complex composites or functionally graded materials by infiltrating particulate phases into porous ceramics (Anne, Vleuglel, and Van der Biest, 2006) and to facilitate putting uniform mineral coatings on metal for enameling (Boccaccini et al., 2006). This technique depends on using a potential field to move charged particles that are suspended in a fluid phase. In most cases the thickness of the particle layer is self-limiting as the thickness of the accumulated particulates reduces the movement of electrons. Fabrication generally involves a second step that fixes the layer of particles together and bonds them to the surrounding surfaces. In the case of infiltrated ceramics or coatings for enameling metals; the deposited cake of particulates can be heated to fuse the electrophoretically-transported material into the structure.

Electrophoresis is used to improve Portland cement-based concretes or mortars by transporting nano-particles into pore spaces (Cardenas and Struble, 2006). Fixing or cementing the materials in voids to provide a

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densification step that will bond the resulting composite phases together is a significant problem. An advanced approach is being explored that uses electrophoresis to migrate nano-sized particles into concrete and uses a solution or gel phase that can react with the particulates to produce cementation in the pore space in the mortar or concrete to bond the new composite together. The goal of this report is to explore two approaches that can produce new composites that contain both electrophoretically infiltrated particulates and a cementing reaction that can bind the particulates in the matrix.

One set of mortar samples was infiltrated with nanoparticle silica fume and the cementation reaction used a sodium silicate cementation reaction. A second set used nanoparticle silica fume and a sodium silicate/aluminum nitrate cementation reaction. A third set was infiltrated with nano-sized crystals of calcium carbonate and cemented using a calcium carbonate precipitation system.

2. METHODS AND MATERIALS

Mortar cubes cast using the ASTM C109 procedure (ASTM, 2007) were selected as the experimental medium to be treated using electrophoresis and electro-transport techniques. Three types of mortar were prepared using the preparation and proportioning specified in ASTM C 109. Two different cube compositions were used (Table 2). All samples were cured for 28 days and then diamond sawed to make samples that were 50 mm by 50 mm and a nominal 10 mm in thickness.

An electrophoresis/electro-transport cell was constructed from polyethylene and the samples were mounted in the cell using silicone cement. Graphite electrodes were used to apply a DC voltage (6 to 12 volts) across the cell (Fig. 2).

Treatment A involved the electrophoretic transfer of silica fume from a suspension of 10 grams of silica fume (Elkem EMS-970D) in 500 ml of distilled water containing 20 ml of sodium silicate ($\text{SiO}_2/\text{NaO}_2 = 3.2$). The suspension was placed on both sides of the mortar plate. A DC voltage of 6 volts was applied across the sample for 4 hours. Current flow varied from 2 to 4 mA.

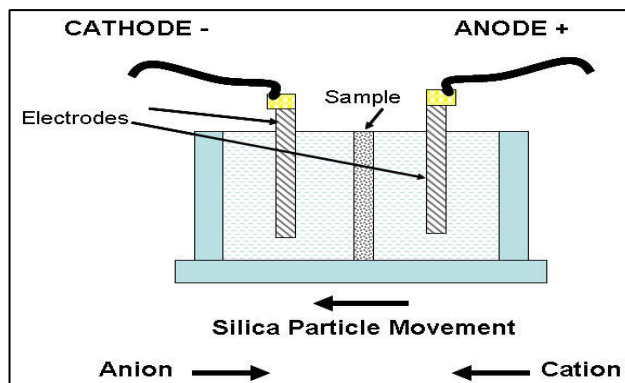


Fig. 2. Sketch of test cell for electrophoresis/electro-transfer in mortar samples.

Treatment B involved the electrophoretic transfer of silica fume supplied as a suspension of 10 grams of silica fume in 500 ml of a solution containing 20 ml of sodium silicate, 50 grams of sodium hydroxide and 95 grams of aluminum nitrate. Cell operation was similar to previous treatment.

Treatment C consisted of electrophoretic infiltration with nano-sized nuclei of calcite followed by electro-transport of calcium from a 10% calcium acetate solution placed in the anode side of test cell. A 10% ammonium carbonate solution was placed in the cathode side of the test cell. Cell operation was unchanged but current ranged from 3 to 4 mA.

The surface morphology of the test samples was characterized as to morphology using both optical microscopy and scanning electron microscopy. The optical imaging was done using a Nikon SMU-Z binocular microscope equipped with a CoolSNAPpro digital image acquisition system (Media Cybernetics). The electron microscopy was done using an Electroscan Environmental Scanning Electron Microscope (ESEM) Model 2020 with a lanthanum hexaboride (CeB_6) electron source and a gaseous secondary electron detector (GSED). The imaging conditions employed an accelerating voltage of 20 KeV and 1.81 mA, and approximately 5 Torr (666 Pa) water vapor in the sample chamber. The environmental gas was vaporized distilled water supplied via a digitally controlled needle valve assembly contained in a sealed located outside the sample

Mortar Type	Treatment	Initial Density (g/cm^3)	Final Density (g/cm^3)
Portland Type I	Silica Fume	1.67	1.71
Portland Type I	Silica + Al Nitrate	1.88	1.89
Portland Type I	Carbonation	1.87	1.98
Portland + Fly Ash	Silica Fume	1.77	1.82
Portland + Fly Ash	Silica + Al Nitrate	1.89	1.91
Portland + Fly Ash	Carbonation	1.99	2.01

chamber. Erlenmeyer flask Images of these samples were collected over a period of 30 seconds, and stored as 1 MB TIF files.

The crystal structure of the coating was determined using the Philips PW1800 Automated Powder Diffractometer system. The run conditions included use of $\text{CuK}\alpha$ radiation and scanning from 2 to $65^\circ 2\theta$ with collection of the diffraction patterns accomplished using PC-based Windows versions of Datascan (Materials Data, Inc.) and analysis using Jade.

3. RESULTS

3.1 Changes in the Density of Treated Mortar Samples

The data on the density changes observed in treated and untreated samples are presented in Table 2. The greatest change in density was observed in the Portland cement-based mortar with no fly ash when it was carbonated (Fig. 3.).

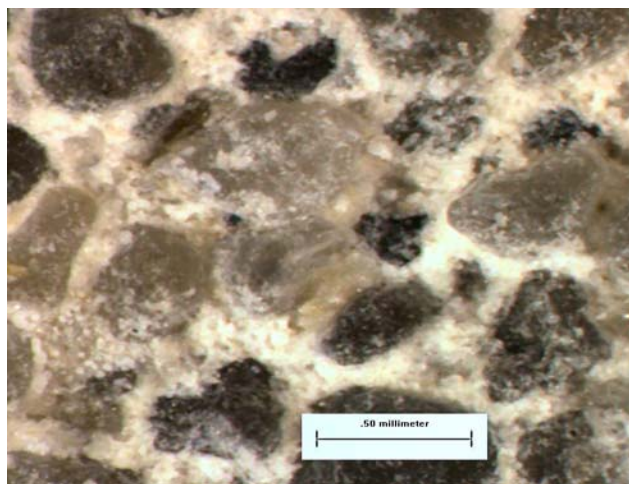


Fig. 3. Photomicrograph of Portland cement mortar after carbonation treatment. Note that the major voids are filled with calcite crystals.

Figure 4 shows the mortar before the carbonation treatment.

Examination of the surface of a carbonated mortar sample under the SEM shows a coating of fine spheres of acicular crystals of calcite (Fig. 5).

3.2 Void Fillings of Treated Mortar Samples

The sodium silicate silica fume void filling materials are amorphous gels and cannot be characterized using X-ray diffraction. In the case of the carbonation treatment, X-ray diffraction patterns were obtained in order to determine what crystalline polymorphs of

calcium carbonate were present in the void filling (Figs. 6 and 7). Examination of both of the carbonated samples, (mortar samples with and without fly ash addition) showed that primarily calcite had formed. Small peaks characteristic of aragonite indicated a trace amount of aragonite has formed in the treated mortar made without fly ash.

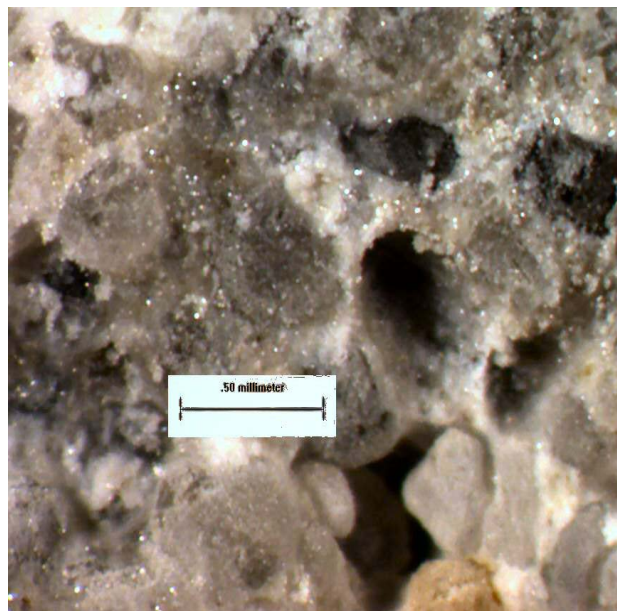


Fig. 4. Photomicrograph of untreated portland cement-based mortar. A normal pattern of voids is apparent.

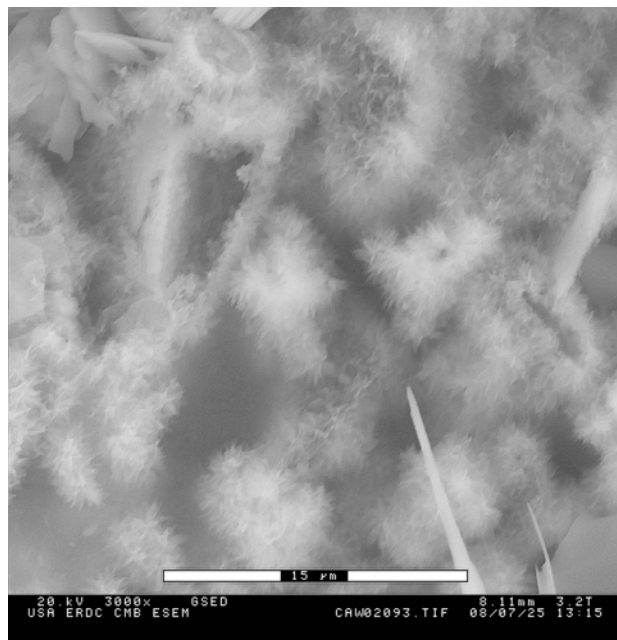


Fig. 5. SEM photomicrograph of the surface of a carbonated sample.

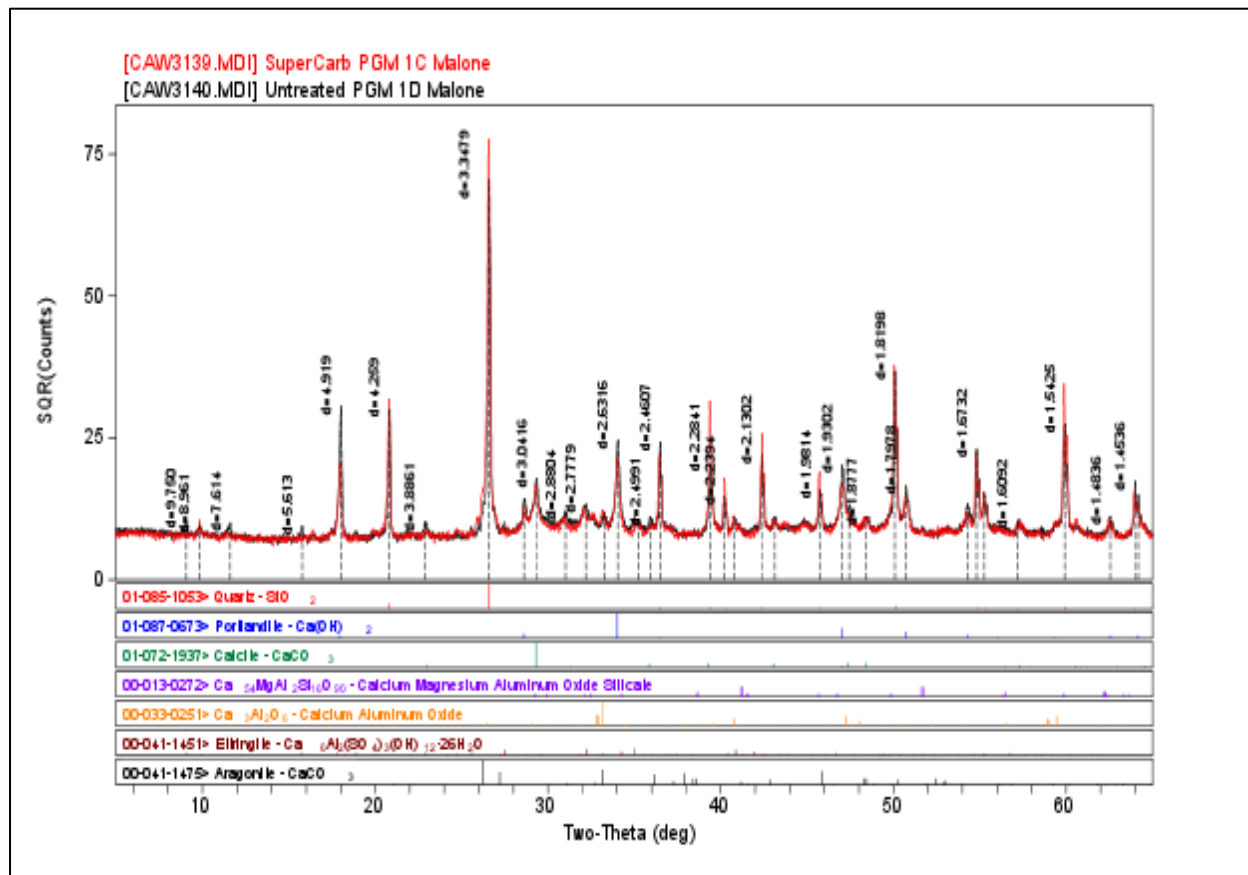


Fig. 6. X-ray diffraction pattern from carbonated Portland cement mortar sample. Note the principal carbonate is calcite. Aragonite is present in trace amounts.

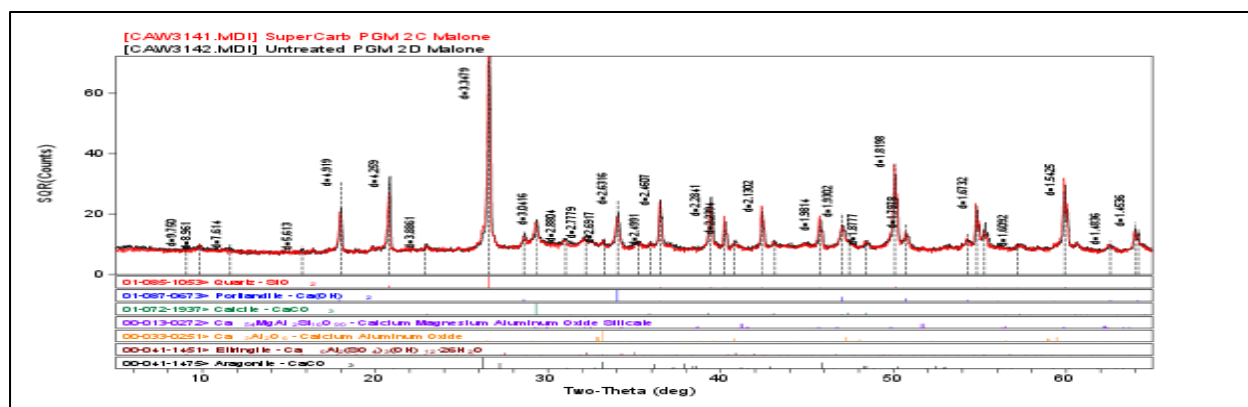


Fig. 7. X-ray diffraction pattern from carbonated Portland cement mortar sample containing fly ash. Note the principal carbonate is calcite.

CONCLUSIONS

The investigation of electrophoretic approaches to void-filling in mortars has shown the following:

a) Both the silica-based and the carbonate-based infiltration systems worked to the extent that the treated density observed was greater than the initial density,

b) The carbonation system used to treat the Portland cement-based mortar showed the greatest overall change in density,

c) Examination of the carbonation product indicates it is primarily calcite but aragonite can be an additional product, and

d) Carbonation may offer significant advantages over electrophoresis alone in that it migrates in crystallization nuclei electrophoretically and then uses electro-migration to move in reagents that can precipitate phases that both fill voids and cements itself in place.

Inorganic cements such as carbonates have been widely observed to form strong structural elements in biological systems. Research into using electrophoresis/electro-transport system to add structurally useful polymorphs, such as fibrous aragonite, to a cemented matrix may provide valuable new bio-mimetic composites.

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